Metal-Based High Capacity Li-Ion Anodes

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Project ID #
ES063

Overview

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Timeline

- Project start date: 01-01-2011
- Project end date: 12-31-2014
- Percent complete: 80%

Barriers

- Barriers addressed
  - Lower-cost
  - Higher volumetric capacity and
  - Abuse-tolerant safer anodes

Budget

- Total project funding
  - DOE $724,626
  - Contractor share: Personnel
- Funding received
  - FY13: 172k$
  - FY14: 172k$

Partners

- National Laboratories
  - Brookhaven; Argonne; Lawrence Berkeley
- Local Industry
  - Primet
- Academia
  - Other Anode Partners

Relevance and Objectives of Work

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- **The primary objectives of our work are to:**
  - Increase the volumetric capacity of the anode by a factor of two over today's carbons
    - 1.6 Ah/cc
  - Increase the gravimetric capacity of the anode
    - $\geq$ 500 Ah/kg
  - Lower the cost of materials and approaches
  - Be compatible with low cost layered oxide and phosphate cathodes and the associated electrolyte
- **The relevance of our work is:**
  - Achieving the above objectives
    - Will increase the cell energy density by up to 50%.
    - Will lower the cost of tomorrow's batteries

Relevance: Milestones

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a) Determine the reaction mechanism of the nano-Sn-Fe-C system. (Sept. 13) **Completed**

b) Identify the cause of the first cycle excess charge capacity and propose approaches to mitigate it. (Sept. 13) **Completed**

c) Identify an anode candidate having an energy density of 2 Ah/cc for at least 100 cycles (Sept. 2013) **Completed**

d) Determine the electrochemistry of the leached nano-silicon material, and compare to the standard silicon. (Sept. 13) **Completed**

e) Identify the two most promising approaches for nano-silicon. (Dec. 13) **Completed**

f) Reduce the first cycle excess capacity to less than 20% for nano-tin. (Mar-14) **Ongoing**

g) Go/No-Go: Decision on solvothermal approach for nano-tin. Criteria: Identify the optimum synthesis approach for nano-tin anode material. (Jun-14) **Completed - no-go on solvothermal**

h) Achieve more than 200 cycles on nano-tin at double the capacity of carbon at the 1C rate. (Sep-14) **Ongoing**

Approach and Strategy: Improved Anodes

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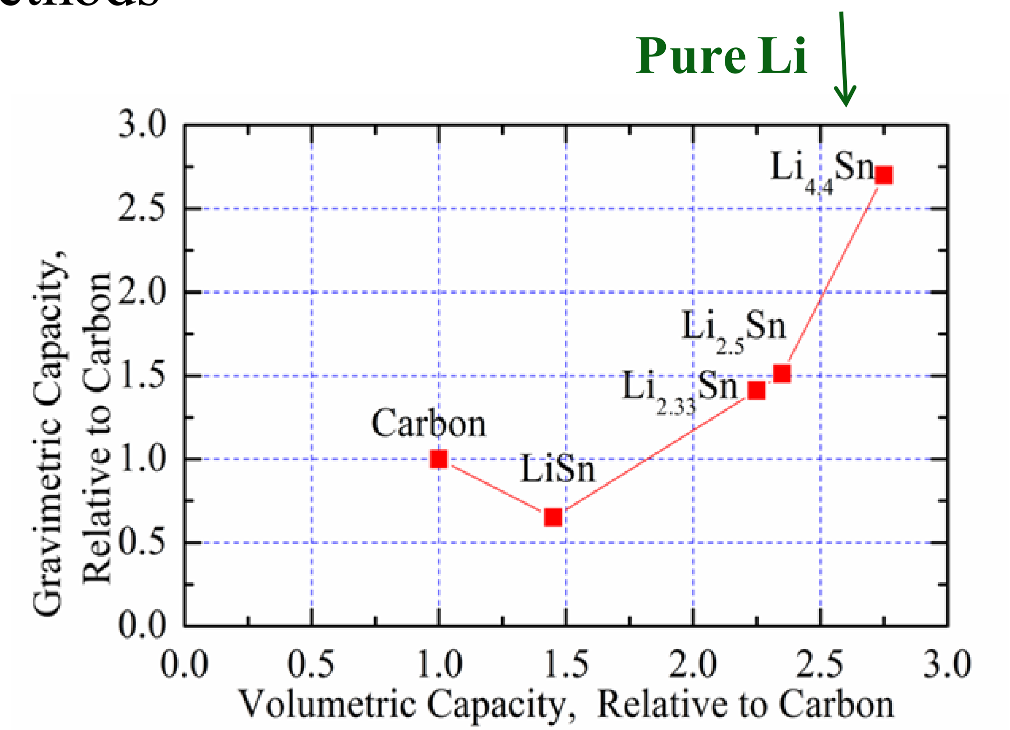
- Place emphasis on low cost materials, tin and silicon
  - Study modified tin initially
    - Safer than silicon
  - 2 Li/Sn doubles capacity
  - Find several simple synthesis methods
    - Nano-amorphous tin
    - Need low cost components
  - Protect the nano-tin
    - From side reactions



Volumetric capacity of Li≈$Li_{4.4}Sn$≈$Li_{4.4}Si$

Technical Accomplishments: Barriers being Addressed

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- **High Cost**
  - Find a tin-based anode, that does not contain cobalt
    - Low cost materials
    - Low cost manufacturing method
- **Low Volumetric Capacity of Li-ion batteries**
  - Volumetric capacity of Li-ion batteries limited by carbon anode
  - Find a material with double the volumetric capacity
- **Low Safety and Abuse-tolerance**
  - Find an anode that reacts with lithium faster
    - Minimizes risk of dendrite formation

Milestone (a) – Reaction mechanism of Sn anode
Sn oxidation state changes reversibly

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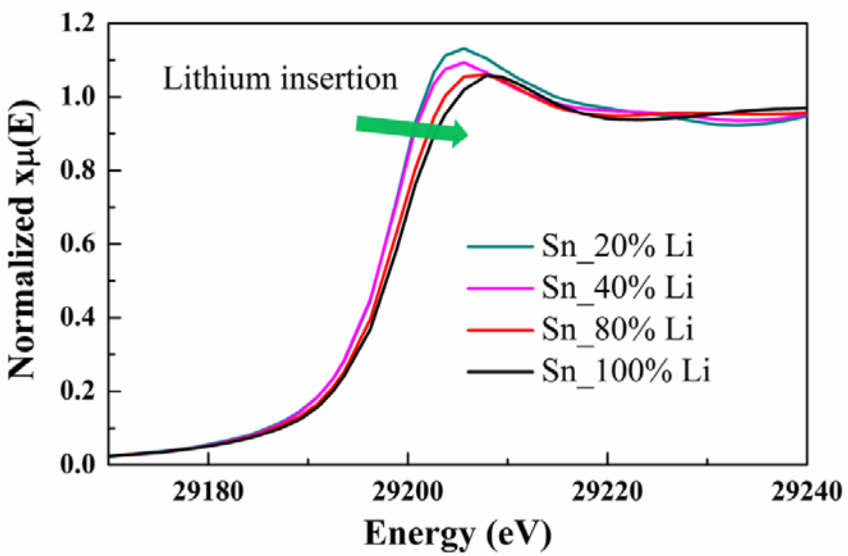
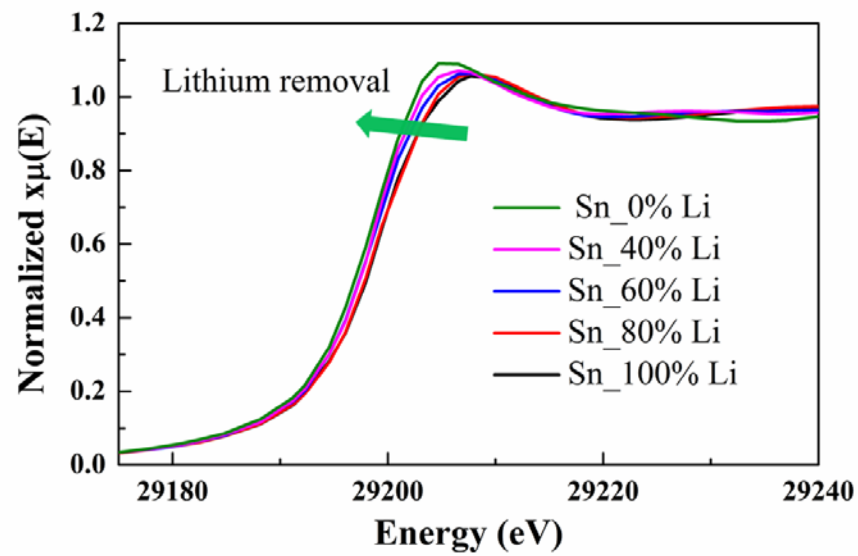
- **Mechanochemical synthesized Sn-Fe-Ti-C***
  - Absorption edge energy shift observed in Sn K-edge XANES
  - Oxidation state of Sn undergoes a reversible change during the lithiation/delithiation process.





- *Ti reduction of SnO in presence of Fe and C in grinding mill
  - Ti determined as preferred reducing agent (see 2013 report)
- Measurements made at Brookhaven National Laboratory

Milestone (a) – Reaction mechanism of Sn anode
Li reaction with Sn_2Fe is reversible

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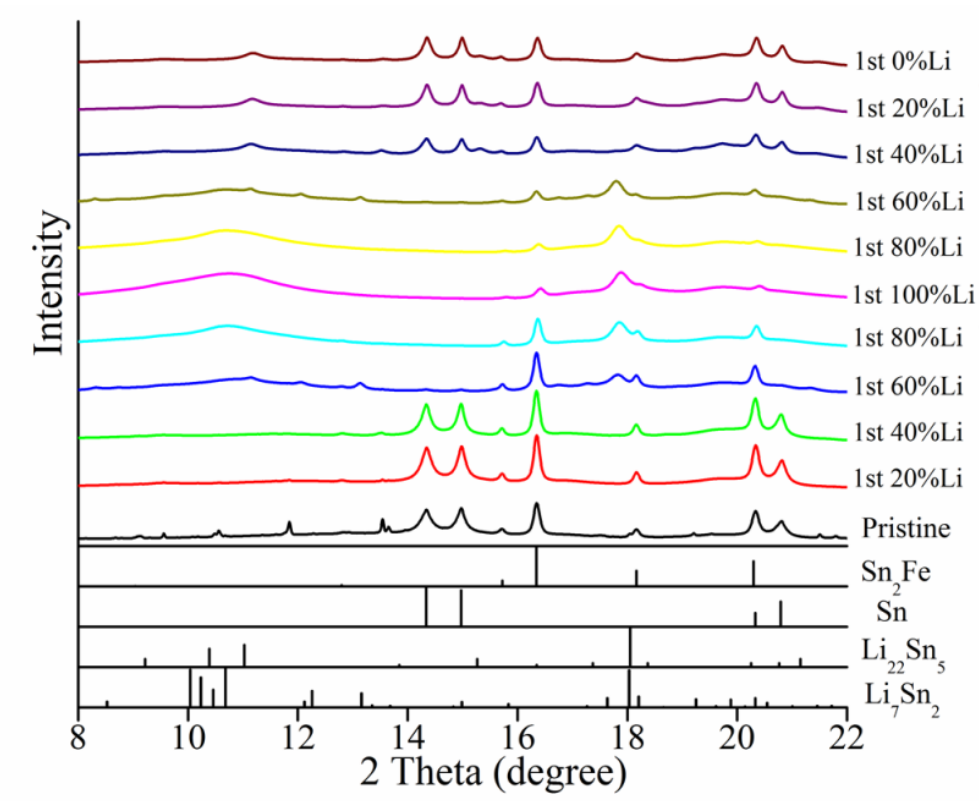
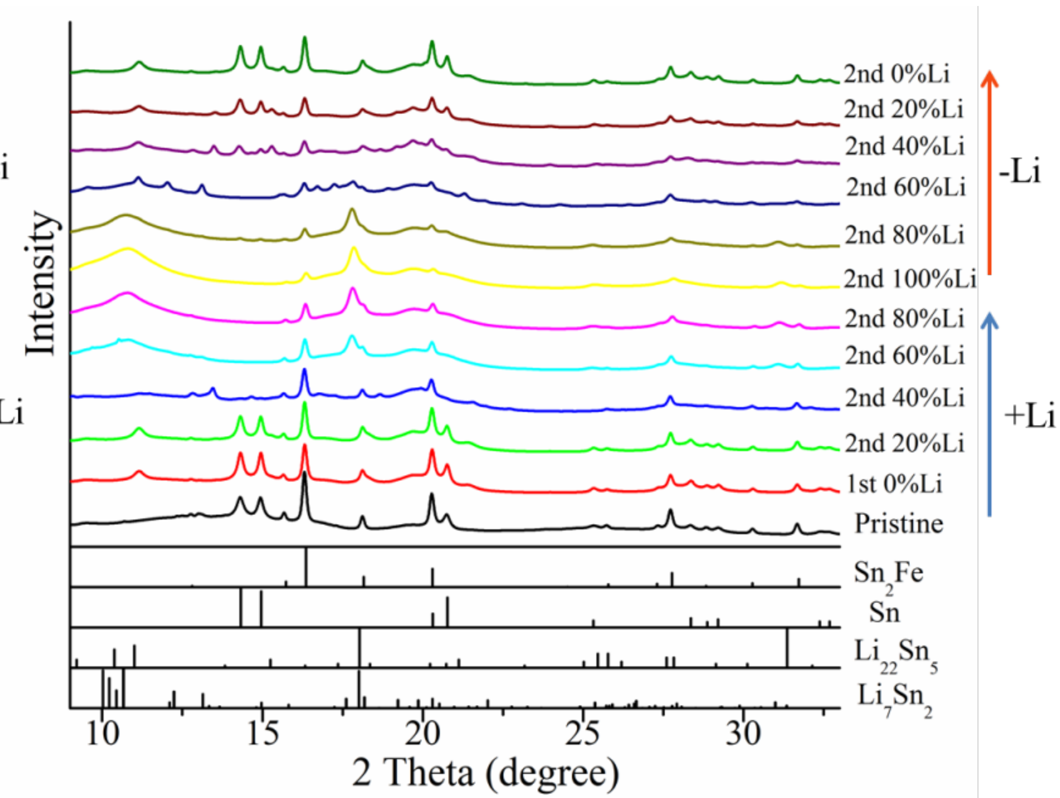
X-ray diffraction shows the presence of Sn and Sn_2Fe in initial electrode, their disappearance on lithiation and their reformation on lithium removal



1^{st} cycle (λ= 0.728 Å)



2^{nd} cycle (λ= 0.727 Å)

Milestones (a) & (b) – Reaction mechanism of Sn anode
Mixture of phases with some irreversible solids formed

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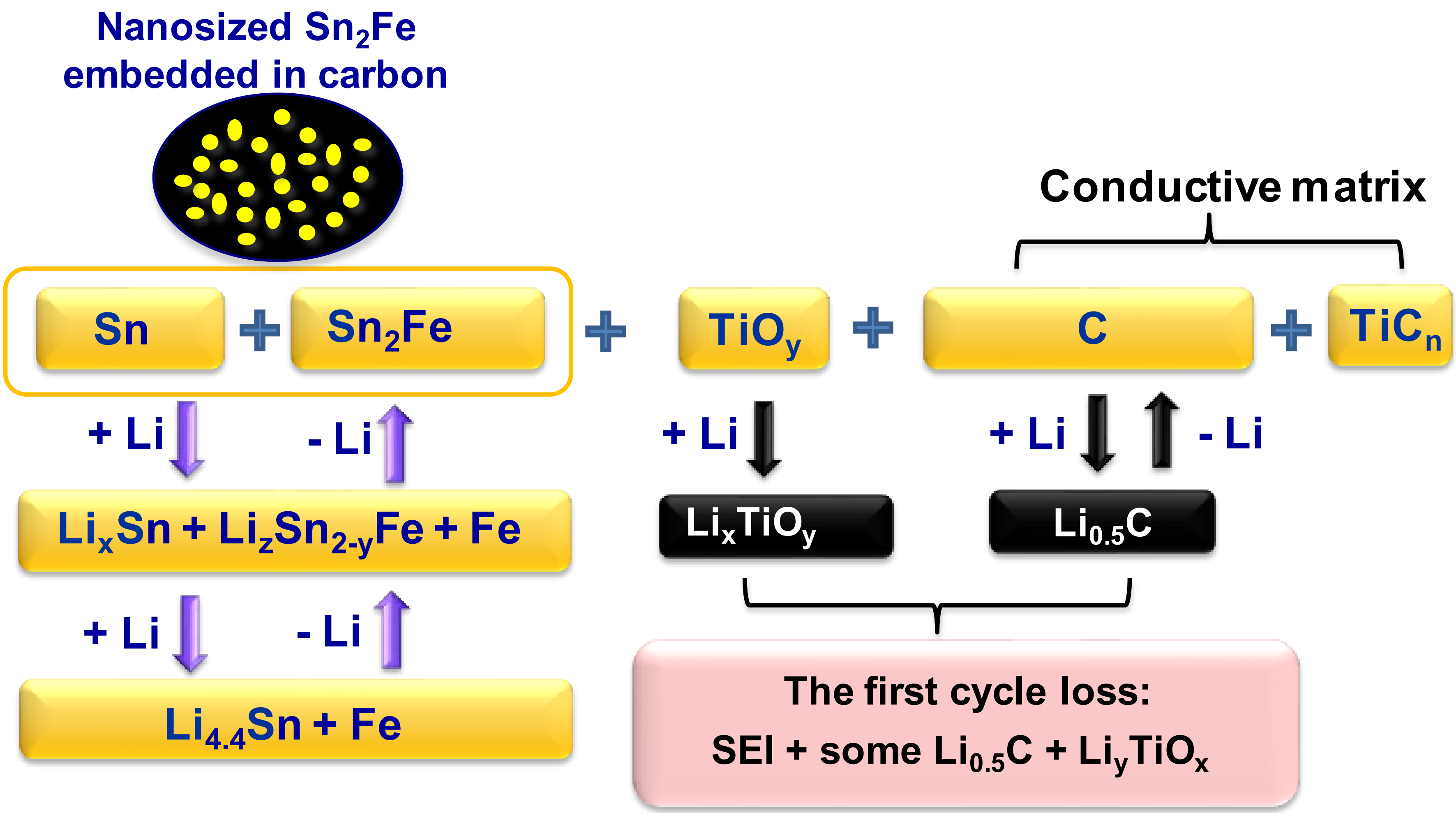

Cause of 1st cycle loss (excess capacity)

- SEI on reactive interfaces
- Formation of lithium titanium oxides (lithium not recovered within voltage window)
- Formation of lithium-rich carbons, e.g. $Li_{0.5}C$

Milestone (f) - Reduce first cycle excess capacity
Impact of titanium content

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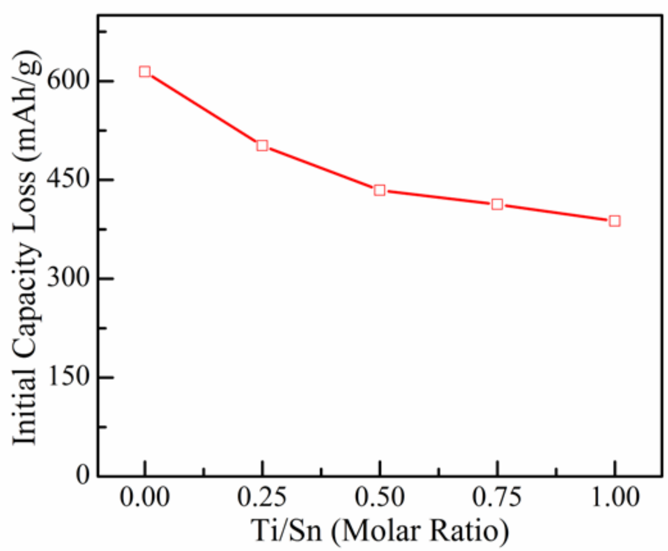
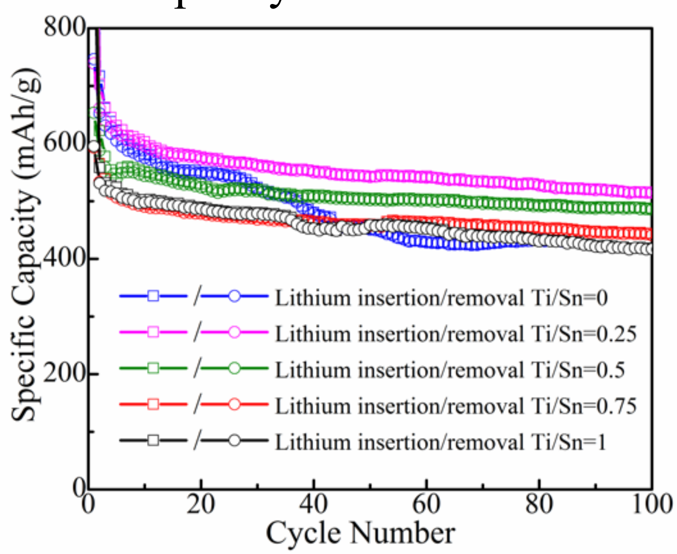
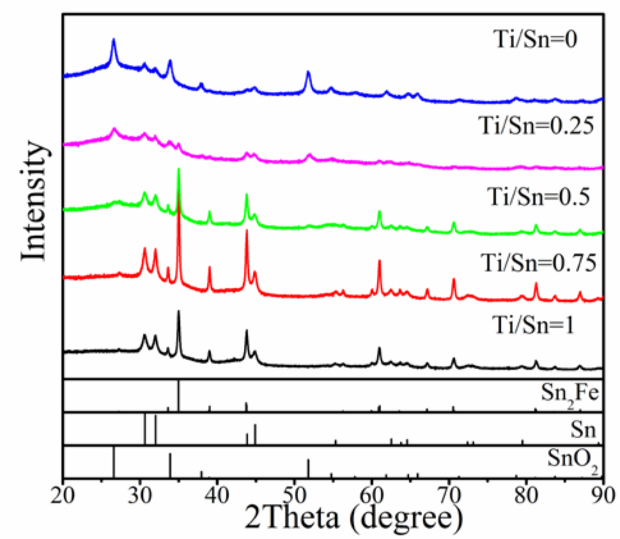
- **Ti/Sn ratio in mechanochemical synthesis**
  - The presence of titanium content reduces the first cycle excess capacity
    - As the Ti/Sn ratio increases from 0 to 1, the first cycle capacity loss decreases from 610 mAh/g to 390 mAh/g
    - This decrease mainly occurs as Ti/Sn ratio increases from 0 to 0.5
      - 0.5 Ti/Sn required to reduce the SnO, but carbon may also be a reductant
  - From an overall capacity retention point of view, the optimum Ti/Sn ratio appears to be between 0.25 and 0.50
    - Ti/Sn ratio ≥ 0.75, the reversible capacity decreased
    - Ti/Sn ratio = 0.25: amorphous, good reversible capacity and capacity retention
    - Ti/Sn ratio = 0: the lowest capacity retention







Milestone (f) - Reduce first cycle excess capacity
Impact of graphite content

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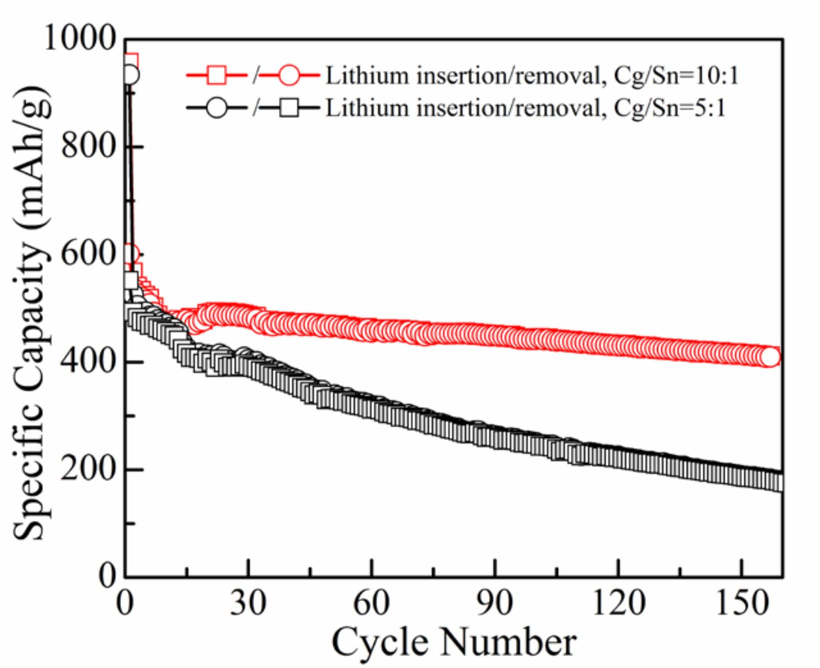
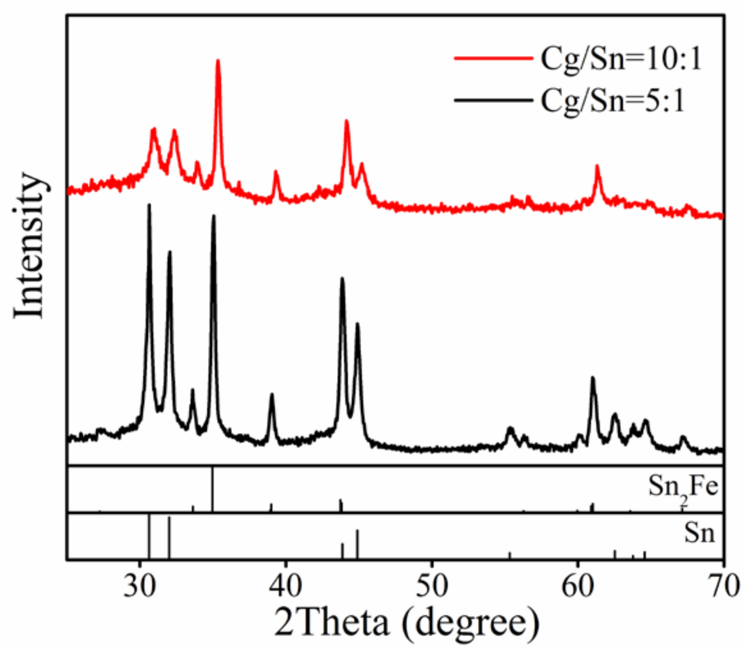
- **Graphite/Sn ratio in mechanochemical synthesis**
  - Although graphite contributes to the first capacity loss, the overall electrochemical performance is significantly reduced when the carbon content is halved.
    - Carbon plays a critical role in maintaining the capacity on cycling, and its reduction is not recommended
    - Less carbon leads to larger amounts and greater crystallinity of elemental tin





Milestone (c) - Identify an anode candidate having an energy density of 2 Ah/cc for at least 100 cycles

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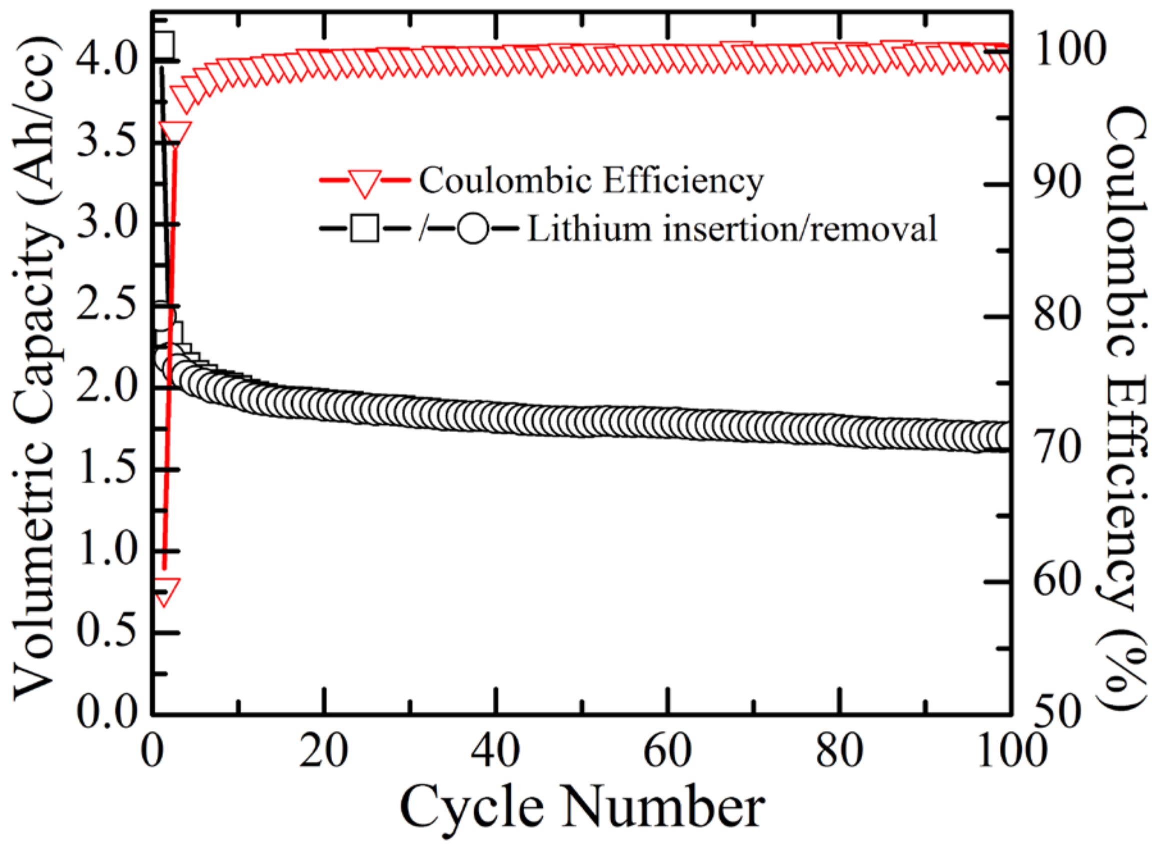
- **Mechanochemical synthesized Sn-Fe-C**
  - The nano-sized Sn-Fe-C composite has a volumetric capacity of ~1.6Ah/cc after 100 cycles
    - Good candidate to achieve 2 Ah/cc
  - Good capacity retention up to 100 cycles



Milestone (g) - Identify optimal synthesis approach for nano-tin; Solvothermal a no-go based on capacity fade

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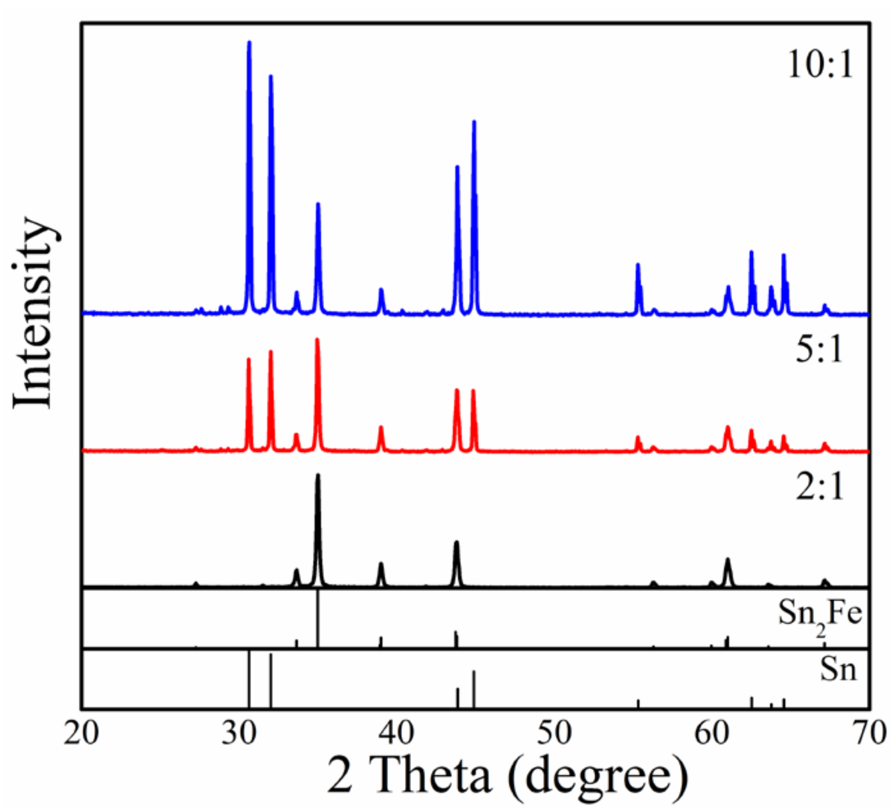
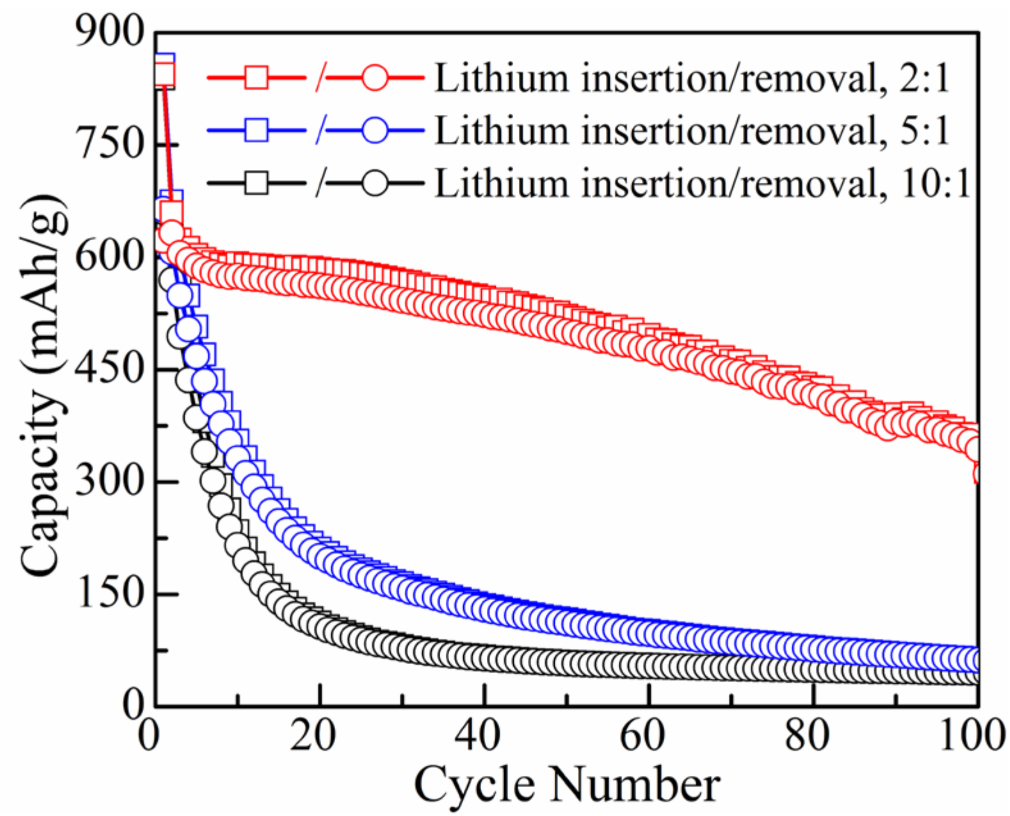
- **Solvothermal synthesis of Sn-Fe composite**
  - The capacity fades on cycling for all Sn:Fe ratios, even when only the Sn_2Fe phase is present.
  - The fading is extreme when metallic tin is present, as observed by X-ray diffraction.
  - Not competitive with mechanochemical, so no-go on solvothermal.





Milestone (d): Leached nano-silicon
Background information on Si-Al alloy

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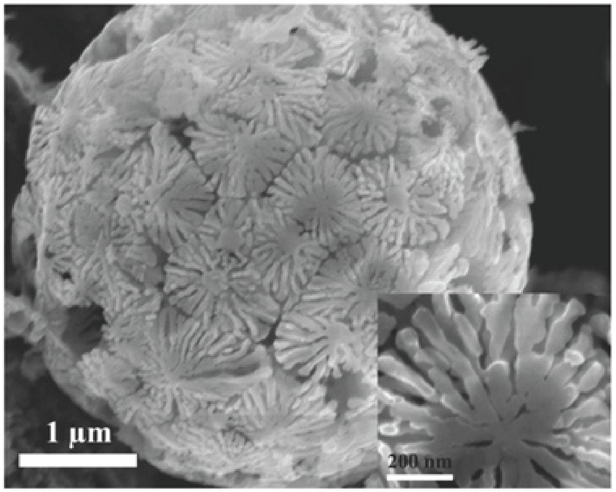
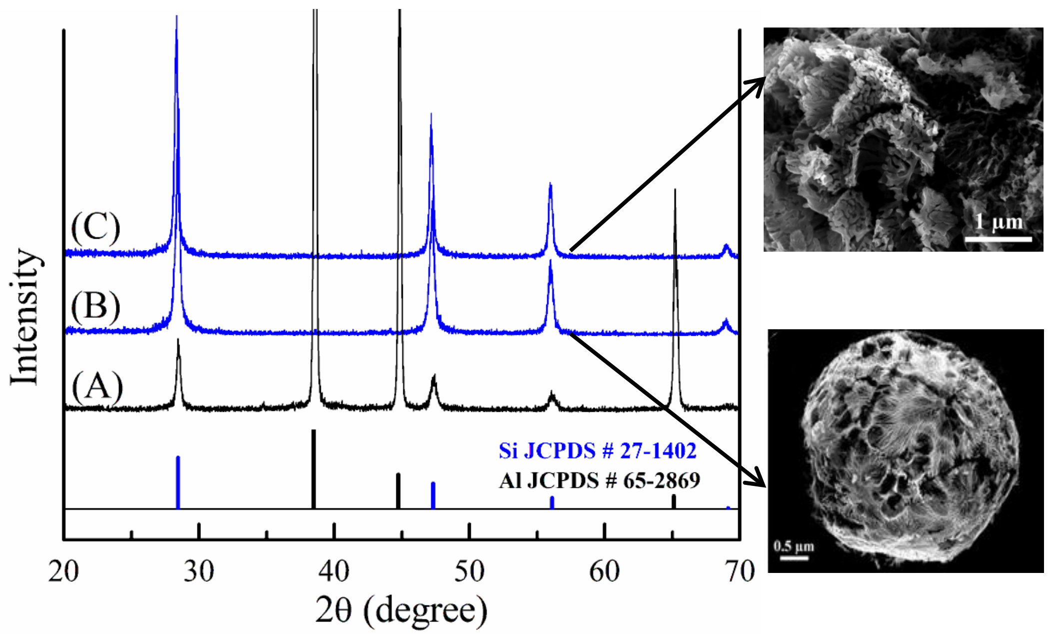
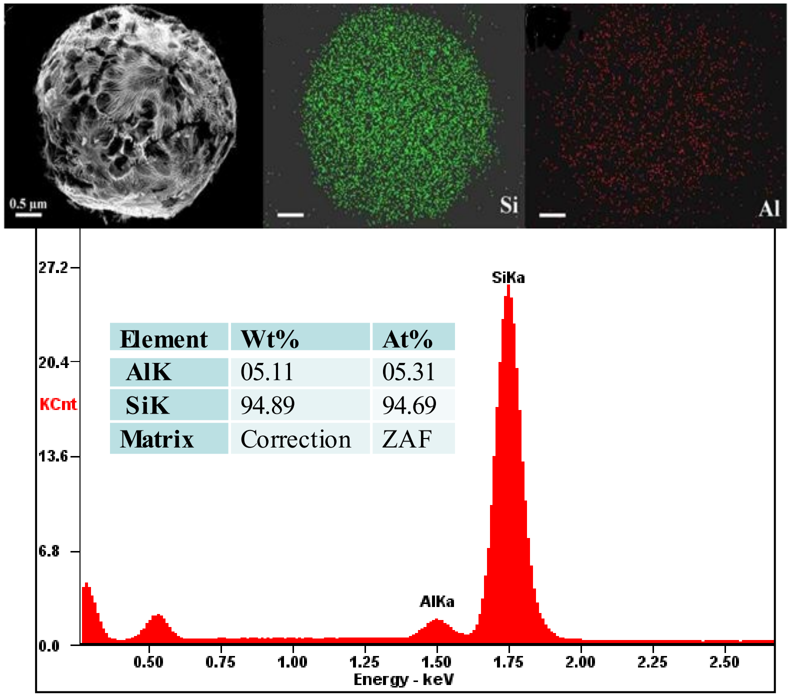
- **Synthesized from commercial quenched alloy**
  - Etching Al-Si alloy
    - Gives porous Si with 3D network
    - XRD data yields a lattice parameter larger than pure Si
    - EDS ~5 wt. % Al uniformly distributed in this material
      - 3 % in solid solution, remainder on surface

MRS Commun., 1, 119-121 (2013)





(A) Al-Si, (B) Si spheres and (C) broken Si spheres.



Element	Wt%	At%
AlK	05.11	05.31
SiK	94.89	94.69
Matrix	Correction	ZAF

Milestone (d) - Determine the electrochemistry of the leached nano-silicon; compare to the standard silicon.

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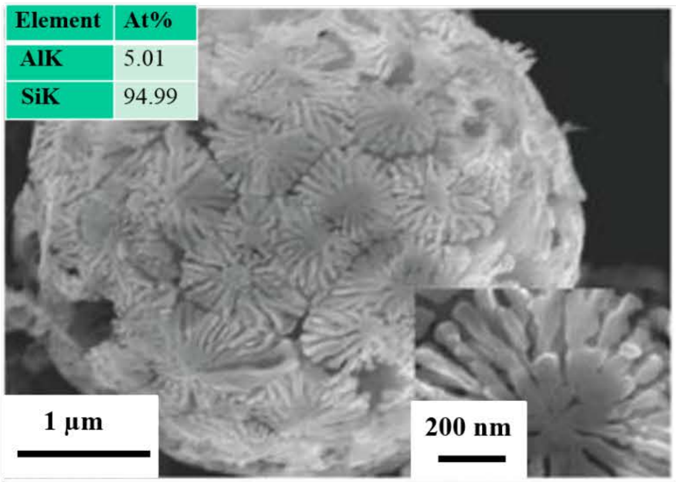
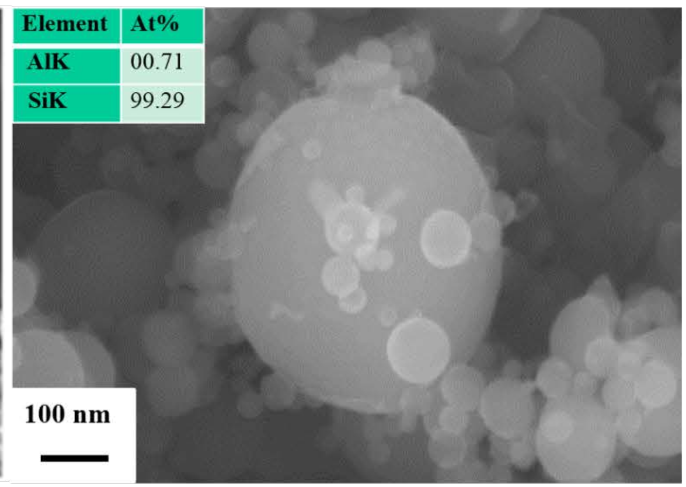
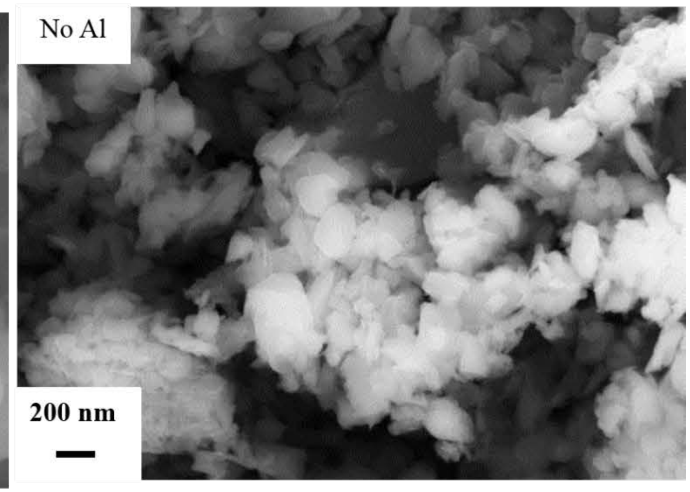
Morphology of the three silicon materials



Leached Si



Standard Si



Company Si

- Leached Si are spheres with clear flower-like morphology
- Standard Si are solid-shell spheres with different sizes
- Company Si are like cubes aggregated together

Milestone (d) - Determine the electrochemistry of the leached nano-silicon, and compare to the standard silicon

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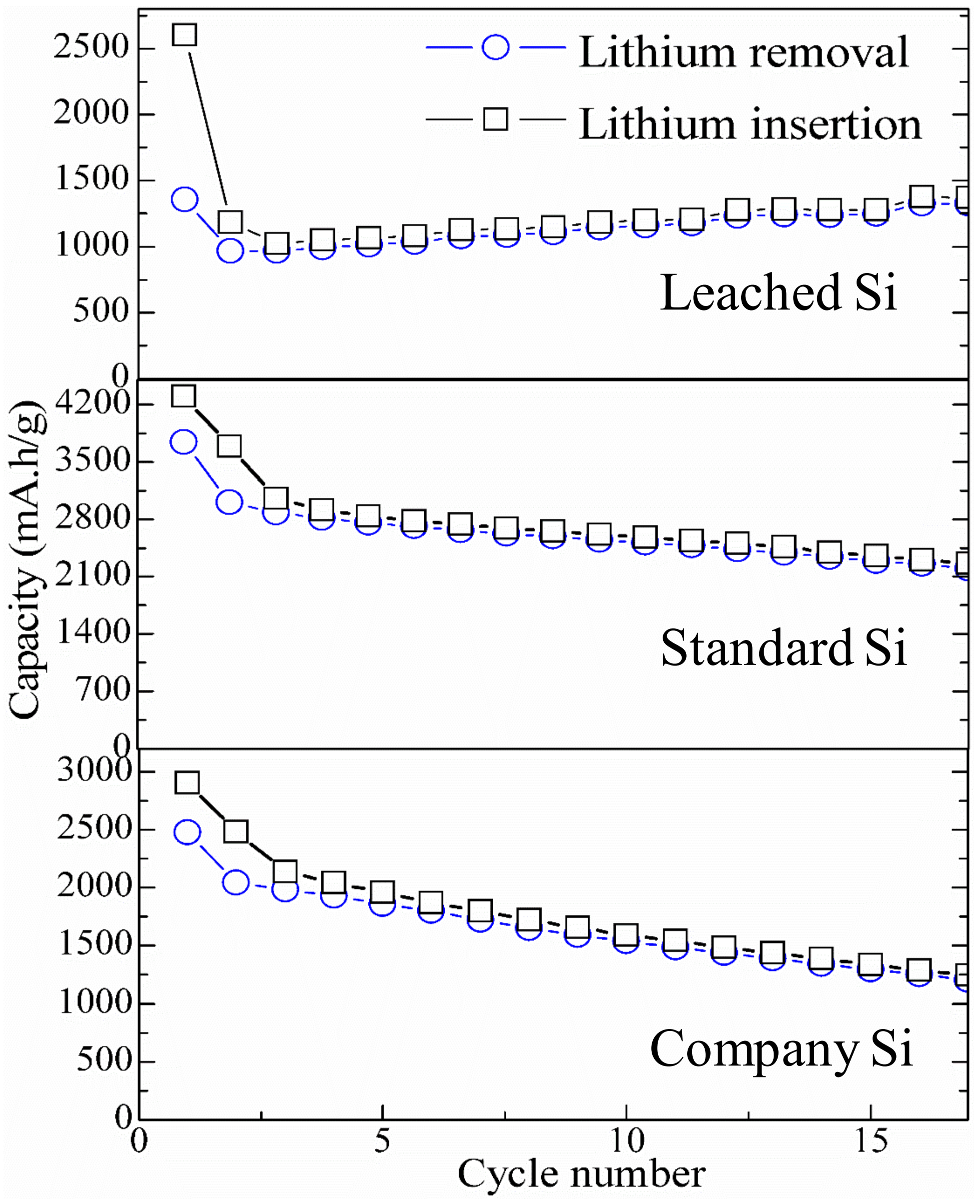

-The leached nano-silicon possesses a good capacity stability, which attains 1350 mAh/g after 18 cycles and is still growing; the standard silicon has a high capacity up to 2300 mAh/g but fades gradually; the third-party provided silicon behaves similarly with a capacity of 1250 mAh/g after 18 cycles.

-Testing protocol: 0.12 mA (~C/40) for the first cycle, followed by 0.5 mA (~C/10) for the remaining cycles in a potential range between 0.01 V and 2 V.

Milestone (e): Identify two most promising approaches for nano-silicon

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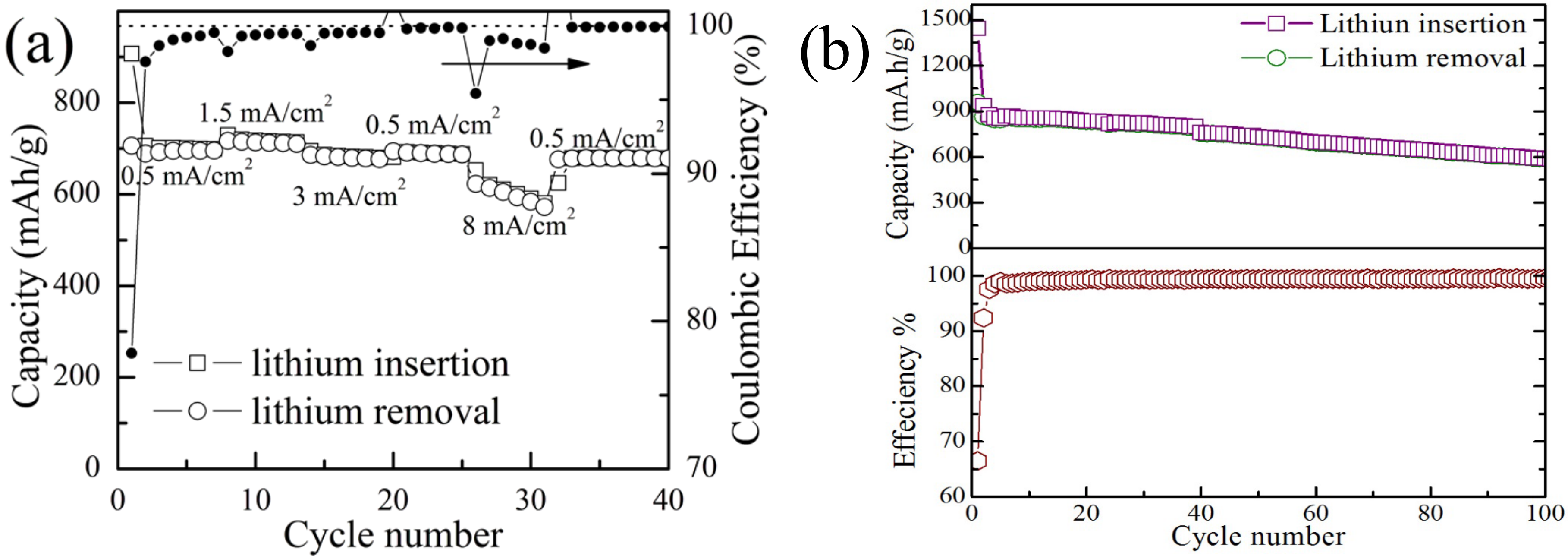
- **Method 1: Leached Si** (described above)
- **Method 2: Metal reduced "SiO"**
  - Si/MgO/graphite (SMOG) composite (reported last year)
    - Very stable, high rate but capacity low
  - Si/TiO_y/graphite composite
    - shows higher capacity



(a) Rate capability and cycling efficiency of SMOG electrode between 0.01 and 1.5 V, and (b) capacity and efficiency versus cycle number of Si-Ti-C between 0.002 and 2 V at C/20 rate (0.4 mA/cm²).

Response to 2013 Reviewers' Comments

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Comments

1. **Approach:** All the reviewers commented positively, noting that the PI had recognized the key issues and was addressing them "demonstrating a variety of techniques…thus mitigating the risk that nothing will work". One reviewer questioned the premise that these anodes "would be safer than carbon-based materials"

   Response: The PI thanks the reviewers for their positive comments. These tin and silicon-based materials should be much safer than carbon because they will not produce any gases on thermal runaway thus reducing pressure build-up. In addition, per lithium stored both Sn and Si release 10 times less energy than carbon on oxidation. Sn releases slightly less energy than Si on oxidation but has a lower melting point. [see technical back-up slide 2]

2. **Technical Accomplishment:** Comments included good and excellent progress toward milestones. Two reviewers commented positively on the tin studies. One reviewer praised the work on the "SMOG" anode and wondered why more work had not been done on this material. Another reviewer would like to see a table comparing the properties of Nano-Sn_2Fe versus nano-Si would have been very useful.

   Response: Work is continuing on the SMOG-type anodes, and in particular on using titanium rather than magnesium as the reducing agent. However, most effort continues on the tin material because it offers overall better behavior and further offers an alternative to the large amount of effort by the community on silicon materials. From a volumetric point of view, both of these systems can in principle give the same capacity as lithium electrodes and double that of today's carbons [the volumetric capacity is limited by the size of lithium itself, rather than by the tin or silicon – see slide 5]

3. **Proposed Future Research:** Reviewer 1 "future work proposed was very good". Reviewer 2 liked the use of go/no-go targets, and hoped this would continue. This reviewer would also like to see an increased emphasis on the nano-silicon from low cost Al-Si alloy. Reviewer 3 would like to see "more specifics on how the project team planned to reduce first cycle irreversibility in nano-Si".

   Response: The project included go/no-go targets in the past year, and an increasing emphasis is being placed on the nano-Si. A major emphasis will be placed on reducing the first cycle excess capacity in the next 6 months.

Collaboration and Coordination with other Institutions

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- **Brookhaven and Argonne National Laboratories**
  - Ex-situ and in-situ synchrotron X-ray diffraction, PDF (pair distribution function) and XAS (X-ray absorption) studies
- **Lawrence Berkeley National Laboratory**
  - Working with BATT anode team comparing tin and silicon materials
    - Similar challenges, such as 1st cycle loss, being addressed
  - Umicore nanograin Si material for Si baseline standard
- **Primet Precision (Ithaca Co)**
  - Collaboration underway on nanosizing materials (Nano-scissoring™) and on Si
- **NYBEST** (New York Battery and Energy Storage Technology Consortium)
  - Building collaborations between Industry, Academia, and Government

Remaining Challenges and Barriers

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- **Nano-Sn_2Fe**
  - 1^{st} cycle excess capacity
  - Cost effective synthesis methods
    - Mechanochemical method
      - Find collaborator to determine viability of mechanochemical manufacturing
- **Nano-Si**
  - 1^{st} cycle capacity loss
  - Cycling efficiency
  - Cycling performance

Proposed Future Work

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- **Nano-Sn_2Fe**
  - 1st cycle excess capacity
    - Determine impact of electrolyte
    - Determine impact of carbon-type
      - Graphite converts to active carbon reacting to give LiC_2
      - Why and how?
  - Cost effective synthesis methods
    - Mechanochemical method
      - Find viable source of iron for scale-up, that maintains nano-size
      - Find collaborator to determine viability of mechanochemical manufacturing

- **Nano-Si**
  - Reduce 1st cycle capacity loss
    - Determine impact of different leaching acids
  - Improve cycling performance over 100-200 cycles
  - Continue working with Berkeley team on cycling efficiency

Summary

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- **Nano-tin**
  - Discovered the excellent electrochemical behavior of nano-Sn_2Fe
    - Has capability to double the volumetric capacity of carbon
      - GO for replacement of carbon anode
      - Has superior cycling efficiency than Si
      - Need to understand role of carbon – what is LiC_2?
    - Need to reduce first discharge excess capacity
  - Found mechanochemical synthesis method for nano-Sn_2Fe
    - Need to determine viability of mechanochemical manufacturing

- **Nano-silicon**
  - Formed by two different methods
    - Nano-silicon formed from Al-Si alloy
      - Unique morphology
      - Electrochemical results look promising
    - Nano-silicon formed from SiO
      - Lower capacity

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Technical Back-Up Slides

Calculation of capacity of Sn-Fe-C composite: Volumetric energy density exceeds carbon

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- **Gravimetric capacity:**
  - **Measured reversible capacity of 600 Ah/kg of total composite**
  - **Sn_2Fe contributes 804 Ah/kg of Sn_2Fe**
  - Remainder contributed by carbon
    - Must be C_2Li
      - 1100 Ah/kg
      - Theoretical capacity of 760 Ah/kg for total composite
    - If C_6Li then theoretical capacity is 490 Ah/kg
- **Volumetric capacity:**
  - **Approaches 1.6 Ah/cc, based on above value of 600 Ah/kg**

Safety of Sn and Si anodes relative to carbon: On complete combustion to the oxide

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- **Free energy of formation of oxide:**
  - **-394.36 kJ/mole for C to CO_2**
  - **-519.6 kJ/mole for Sn to SnO_2**
  - **-371.1 kJ/mole for Fe to ½ Fe_2O_3**
  - **-705.5 kJ/mole for oxidation of Sn_2Fe to SnO_2 and Fe_2O_3**
  - **-850.7 kJ/mole for oxidation of Si to SiO_2**
- **Free energy of oxidation per lithium stored:**
  - **-2366 kJ/Li for a carbon anode**
  - **-160 kJ/Li for a Sn_2Fe anode**
  - **-193 kJ/mole for a Si anode**

Assumptions: 6 C/Li and 4.4 Li/Sn or Si
Even if substantial amounts of carbon are used with the Sn and Si anodes, they will still generate less heat than graphite alone